The enhancement of photocatalytic hydrogen production via Ti^{3+} self-doping black TiO$_2$/g-C$_3$N$_4$ hollow core-shell nano-heterojunction

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ABSTRACT

The Ti^{3+} self-doping B-TiO$_2$/g-C$_3$N$_4$ hollow core-shell nano-heterojunction is synthesized via the continuous hydrothermal deposition and sculpture-reduction processes. The results of SEM, XRD, TEM, XPS and FT-IR imply that the B-TiO$_2$/g-C$_3$N$_4$ hollow core-shell nanospheres have been prepared successfully. The photocatalytic activity of the B-TiO$_2$/g-C$_3$N$_4$ nano-heterojunctions remarkably exhibits an enhancement of 18 times and 65 times than that of normal TiO$_2$ and g-C$_3$N$_4$, respectively. Further, the photocatalytic process and the mechanism of the photocatalytic hydrogen production enhancement have been studied, which could be ascribed to the O$_v$-Ti^{3+} in the B-TiO$_2$ and interface nano-heterojunction, that have been proved by the transient photocurrent, PL, EIS and Mott-Schottky plots.

1. Introduction

The hydrogen (H$_2$), with the green-renewability and high energy density, is expected as the most promising candidate in the exploitation of energy resources. To date, lots of inspiring ways have been achieved, such as chemical, physical or electrocatalytic hydrogen production [1–3], etc. Among these researches, the photocatalytic hydrogen production [4,5], owns the clean, cheap and environmental performance, have be the current focus of the hydrogen energy exploitation. So far, lots of materials have been reported with the remarkable photocatalytic hydrogen production performance, such as ZnO [6], MoS$_2$ [7], SrTiO$_3$ [8] or CeO$_2$ [9], etc. Especially the TiO$_2$, with the physical-chemical stability, unique bandgap structure and photochemical activity, has always been the research hotspot [10–12], since it is first reported in 1972 [13].

For such TiO$_2$ system, the lower solar utilization and higher photon-generated carrier recombination would always be the most formidable issues [14,15], and a plenty of efficient methods have been attempted in past decades, including the doping, surface modification, hetero-junction modification or morphological control. Among these, the doping, with the easy preparation and the universality, has been the preferred way [16], including the metal doping, nonmetal doping or ion doping, such as Shi groups have prepared the C-doped TiO$_2$@g-C$_3$N$_4$ nanoheterojunction for enhancing the photocatalytic H$_2$ evolution [17], Collins-Martinez groups have reported the Ag doped TiO$_2$ with

remarkable visible light hydrogen production performance [18], Gao and Yang groups have prepared the N-doped TiO$_2$ nanobelts as a highly visible-light photocatalyst for hydrogen production [19]. All above would be remarkable results. However, compared with the heterogeneous doping, the Ti^{3+} self-doping would provide researchers a new method for modifying the TiO$_2$, which could improve the visible light absorption, structure matching and stability more efficiently [20,21]. Especially, the Ti^{3+} could promote to form a self-hydrogenated shell to reduce the activation barrier of the H$_2$ for enhancing the hydrogen production [22], and series researches have been explored, such as Mao groups have reported the black hydrogenated TiO$_2$ with increased solar absorption for enhancing the photocatalysis [23], Yu groups have prepared the Cr-SrTiO$_3$-modified B-TiO$_2$ (black TiO$_2$) nanotube arrays for improving the photocatalytic performance [24], Peng groups have fabricated a photoelectrochemical sensor for organic compounds via hydrogenated TiO$_2$ nanorod arrays [25], etc. Though above praiseworthy results demonstrate researchers a promising fingerpost [26,27], but how to prepare the Ti^{3+} self-doping B-TiO$_2$ controllably, economically and steadily are still the most important issue [28], and are studied rarely than other ways. Thus, the preparation of the efficient and stable Ti^{3+} self-doping B-TiO$_2$ would be a challenge for the photocatalytic hydrogen production.

On the other hand, the heterojunction modification would be deemed as one of the most efficient ways for ameliorating the high recombination of the photon-generated carrier in photocatalyst. In such

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modification, the photon-generated carriers, driven by the heterojunction, would transfer to the lower conduction band (electrons) and higher valence band (holes), which could improve the separation of the photon-generated carriers efficiently [29], and has been achieved by series of works, including the Ag_3PO_4 deposition [30], Cu_2O modification [31] or ZnS, CdS surface modification [32–34], etc. Especially the g-C_3N_4 (graphite phase carbon nitride), with the remarkable visible light response and hydrogen evolution potential, are considered as ideal materials for photocatalytic hydrogen production or surface modification [35], and have been reported as the current hotspot, such as Kang groups have prepared the carbon quantum dots modified g-C_3N_4 via water splitting for photocatalytic hydrogen production [36], Safaei groups have fabricated the Z-scheme g-C_3N_4/$BiVO_4$ photocatalyst for enhancing the photoelectrochemical water splitting [37], Zhang groups have prepared the interlocking g-C_3N_4/CdS with high efficiency and stable photoelectrochemical hydrogen production [38], Shi groups have prepared the Ag_3PO_4/g-C_3N_4 composite and obtained a remarkable visible light photocatalytic performance [39]. All above would be regarded as the commendable ways for improving the carrier separation.

What's more, the specific surface area is another important factor for photocatalyst, which could prove sufficient reaction sites for improving the photocatalytic process. There, the morphological control would be the most efficient way to ameliorate this characteristic [40], and a plenty of remarkable morphologies have been reported, such as nanoparticles, nanowires, nanotubes or nanosheets [41,42]. Herein, the hollow nanosphere would be a commendable choice, because that the hollow structure could remain multiple reflections for increasing the visible light absorption and the inside-outside walls could provide double specific surface areas for increasing the reaction sites [43], similar researches have been reported in previous literatures, such as Lan groups have prepared the hollow ZnO nanospheres for improving the photocatalytic performance [44], Biswas groups have reported the ZnO_{1-x}/carbondots composite hollow spheres as a remarkable photocatalyst [45], Wang groups have fabricated the hollow Bi_2WO_6 for enhancing photocatalytic CO_2 photoreduction [46], and so on. Thus, the hollow core-shell nanospheres would be identified as a preferential method for regulating the nano-heterojunction.

In this work, we synthesized the Ti^{3+} self-doping B-TiO_2/g-C_3N_4 hollow core-shell nano-heterojunction by continuous two-step hydrothermal deposition and sculpture-reduction processes. Compared with the normal TiO_2 or g-C_3N_4, the B-TiO_2/g-C_3N_4 nano-heterojunction exhibits an obvious enhancement in photocatalytic hydrogen production (about 18 fold of the normal TiO_2 and 65 fold of the g-C_3N_4). Further, the mechanism of the photocatalytic hydrogen production enhancement is studied by the continuous electrochemical testing.

2. Experimental

The Ti^{3+} self-doping B-TiO_2/g-C_3N_4 hollow core-shell nano-heterojunction were prepared via the template method of the depositing with the TiO_2 and g-C_3N_4 continuously, then sculpturing and reducing by the NH_4HF_2 (4 mol/L, 12 h) and NaBH4 (0.5 g, 30 min). The schematic diagram is shown in Fig. 1 and the details are displayed in ESI,
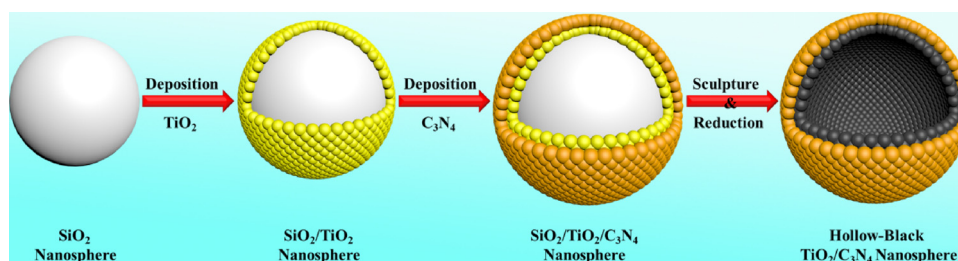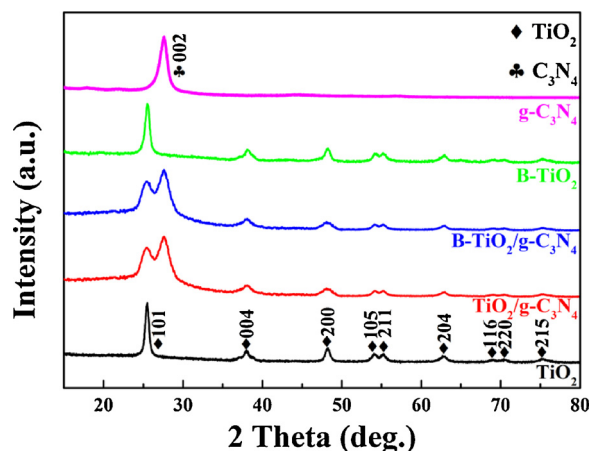
Fig. 2. The XRD of the samples.

including the characterization and photocatalytic activity.

3. Results and discuss

Fig. 2 is the XRD spectra of the samples, including the normal TiO_2, B-TiO_2, TiO_2/g-C_3N_4, B-TiO_2/g-C_3N_4 and g-C_3N_4. As reveled, the diffraction peaks at 25.5, 38.0, 48.2, 54.0, 55.2, 62.9, 68.9, 70.4 and 75.2° could be ascribed to the (101), (004), (200), (105), (211), (204), (116), (220) and (215) planes of the TiO_2 (PDF#21-1272) [26,27]. With the deposition of the g-C_3N_4, the obvious new diffraction peak locates at 27.6° is attributed to the (002) plane of the layer stacking of conjugated aromatic rings on g-C_3N_4 (PDF#87-1526) [29]. It's interesting that, with the reduction, the diffraction peaks of the B-TiO_2 change hardly, including the B-TiO_2 and B-TiO_2/g-C_3N_4, which indicate that the structure of the TiO_2 is stable and is benefit for the continuous photocatalysis. There is no other diffraction peak could be observed, which imply that the core-shell nano-heterojunction is composed of TiO_2 and g-C_3N_4.

Fig. 3 is the SEM of the samples. As shown in Fig. 3a, the as-prepared SiO_2 nanospheres with diameter of about 400 nm are smooth and uniform. Then, with the deposition of the TiO_2 (Fig. 3b) and g-C_3N_4 (Fig. 3c), the surfaces of the samples turn to be rough. Further, with the sculpture and reduction, the hollow core-shell nano-heterojunction has formed and could be observed clearly in Fig. 3d. It's interesting that, in the sculpture-reduction process, the samples could maintain the sphere, which is benefit for forming the hollow core-shell structure. Further, the elemental mappings of the B-TiO_2/g-C_3N_4 nano-heterojunctions are shown in Fig. S1 (ESI). As reveled, the elements of Ti, N and C are distributed on the surface uniformly, which corresponds to the hollow core-shell structure.

In addition, the specific surface area of the B-TiO_2/g-C_3N_4 nano-heterojunctions is calculated by the Brunauer–Emmett–Teller (BET) equation through N_2 adsorption–desorption isotherm measurement [47]. As displayed in Fig. S2a (in ESI), the B-TiO_2/g-C_3N_4 nano-heterojunction, with a specific surface area of 96.80 m^2/g, is a typical

Fig. 1. The schematic diagram of the preparation of the Ti^{3+} self-doping B-TiO_2/g-C_3N_4 hollow core-shell nano-heterojunction.

Fig. 3. The SEM of the samples, (a) SiO$_2$ nanospheres, (b) SiO$_2$/TiO$_2$ nanospheres, (c) the SiO$_2$/TiO$_2$/g-C$_3$N$_4$ nanospheres, (d) B-TiO$_2$/g-C$_3$N$_4$ hollow nano-heterojunction.

hollow core-shell structure. Further, calculated by the Barrett–Joyner–Halenda (BJH) equation, the average size of the pores is about 10.24 nm (in ESI Fig. S2b). All above characteristics are beneficial for improving the photocatalytic performance.

Fig. 4 is the TEM of the as-prepared B-TiO$_2$/g-C$_3$N$_4$ nano-heterojunctions. As displayed in Fig. 4a, the nano-heterojunction with diameter of about 400 nm exhibit obvious hollow core-shell structure. Fig. 4b is the interface of the B-TiO$_2$/g-C$_3$N$_4$, as shown, the g-C$_3$N$_4$ shell covers on the surface of the hollow TiO$_2$ nanosphere, which corresponds to the SEM and is regarded as an important advantage for photocatalysis. Further, the HRTEM of the B-TiO$_2$ and g-C$_3$N$_4$ are shown in Fig. 4c and d, the lattice spaces of 0.350 nm and 0.327 nm are ascribed to the (101) plane of the TiO$_2$ and (002) plane of the g-

C$_3$N$_4$[26, 29,], respectively.

Furthermore, the XPS spectra are performed to illuminate the components and chemical states of the as-prepared Ti^{3+} self-doping B-TiO$_2$/g-C$_3$N$_4$ nano-heterojunction. Fig. 5a presents the full survey, which indicates the presence of Ti, O, C and N in the B-TiO$_2$/g-C$_3$N$_4$ nano-heterojunction. Fig. 5b illuminates the high-resolution spectra of the Ti 2p. As reveled, the two main peaks of Ti 2p$_{3/2}$ and Ti 2p$_{1/2}$ could be fitted into four peaks, that the peaks of 457.7 and 463.6 eV are attributed to the Ti^{3+} 2p$_{3/2}$ and Ti^{3+} 2p$_{1/2}$, the peaks of 458.6 and 464.8 eV are attributed to the Ti^{4+} 2p$_{3/2}$ and Ti^{4+} 2p$_{1/2}$, respectively, which indicate that the Ti^{3+} has formed in the reduction process [27,28]. Further, the O 1 s, revealed in Fig. 5c, could be divided into three peaks of 529.7, 530.6 and 532.2 eV, which could be ascribed to
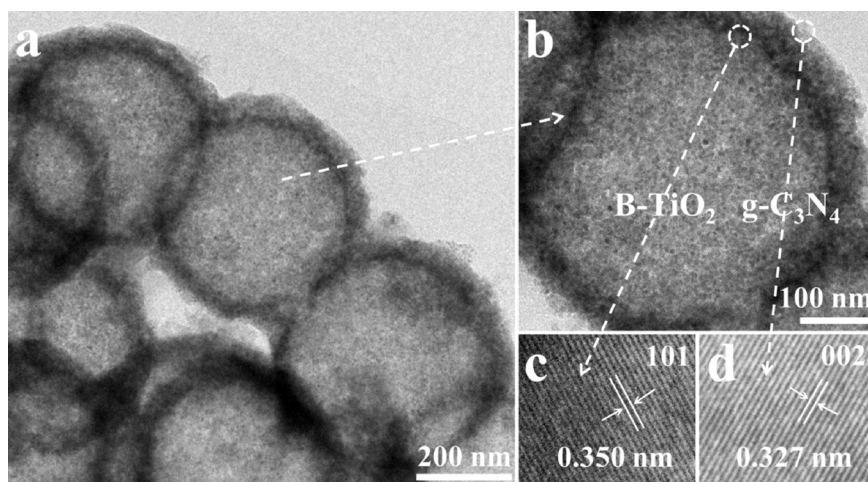

Fig. 4. The TEM of the as-prepared nano-heterojunction, (a) the TEM of the B-TiO$_2$/g-C$_3$N$_4$, (b) the interface of the B-TiO$_2$/g-C$_3$N$_4$, (c) the HRTEM of the B-TiO$_2$ (d) the HRTEM of the g-C$_3$N$_4$.
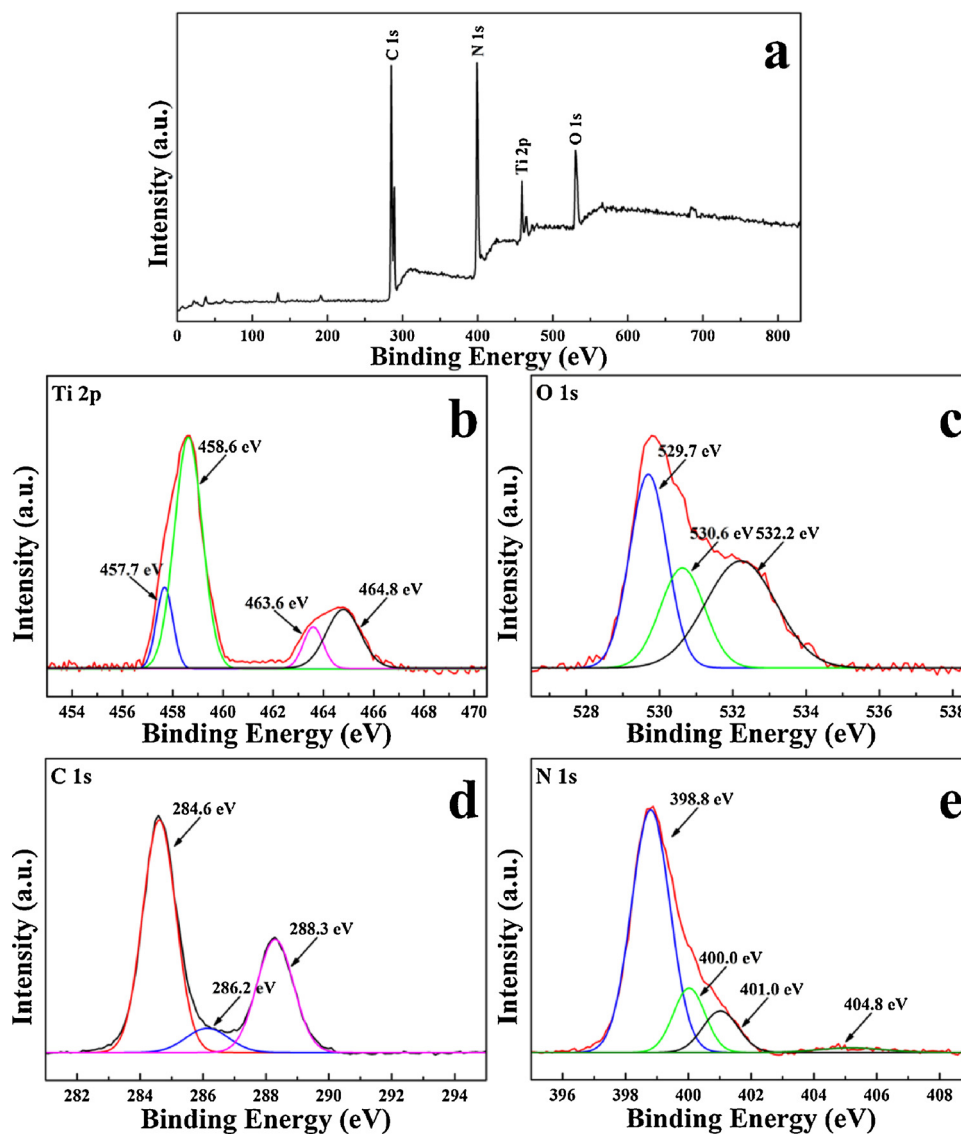
Fig. 5. The XPS of the B-TiO$_2$/g-C$_3$N$_4$ nano-heterojunction, (a) full survey, (b) Ti 2p spectra, (c) O 1 s spectra, (d) C 1 s spectra, (e) N 1 s spectra.

the Ti-O bond in structure, the −OH bond adsorbed on the surface [28,29], and the oxygen vacancy(O$_v$) in the vicinity of Ti^{3+} [22,28], respectively, that could be considered as a convincingly evidence of the presence of Ti^{3+}. Fig. 5d and e are high-resolution XPS spectra of the C 1 s and N 1 s. As revealed in Fig. 5d, fitted by the Gaussian analysis method, the peaks of C 1 s could be divided to three distinct peaks at 284.6, 286.2 and 288.3 eV, which could be attributed to the sp^2 C−C bonds, the C-NH$_2$ species of the g-C$_3$N$_4$ [28,44], and the carbon in N−C═N [29,48], respectively. As illustrated in Fig. 5e, the high re-solution N 1 s spectrum could be deconvoluted into four characteristic peaks. There, the peak at 398.8 and 400.0 are attributed to the sp^2 hybridized nitrogen in the triazine rings (C−N═C) and the tertiary nitrogen N−(C)$_3$ groups [29,48] together with the N−C═N (288.3 eV), respectively. What's more, the peaks locate at 401.0 and 404.8 eV correspond to the free amino groups (C−N−H) and π-excitations[48], respectively.

Furthermore, the FT-IR spectra of the different samples are dis-played in Fig. 6. As revealed, there's no obvious characteristic peak could be observed in normal TiO$_2$, except the 1637 cm^{-1} [28], which could also be observed in all of the samples and ascribed to the hy-droxyl group and physically absorbed water on the surface. With the deposition of the g-C$_3$N$_4$, five new distinct characteristic peaks could be

Fig. 6. The FT-IR spectra of the TiO$_2$, TiO$_2$/g-C$_3$N$_4$, B-TiO$_2$/g-C$_3$N$_4$, B-TiO$_2$ and g-C$_3$N$_4$.

observed, the peaks at 1250, 1325, 1410 and 1569 cm^{-1} could be at-tributed to the aromatic C−N stretching vibration modes, and the peak at 809 cm^{-1} is ascribed to the triazine units [27–29], that correspond to
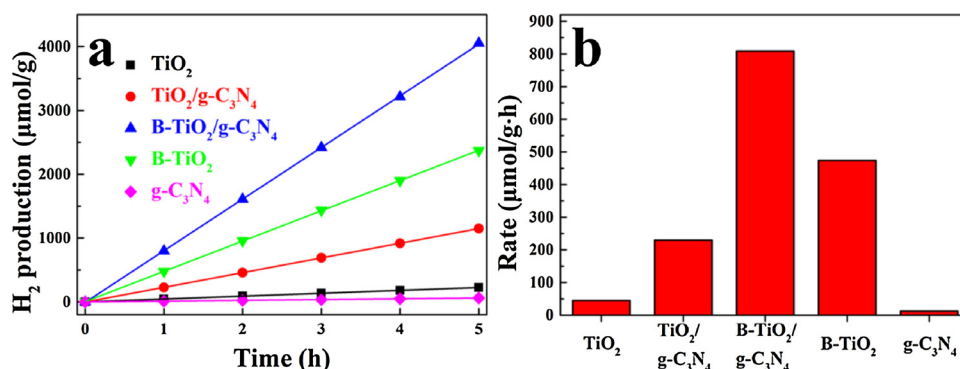
Fig. 7. Photocatalytic hydrogen production activity, (a) the photocatalytic activity of different samples, (b) the histograms of the different samples.

the pure g-C₃N₄ and indicates the modification could affect the structure of g-C₃N₄ hardly. It's interesting that, with the sculpture-reduction process, there is no other new characteristic peak could be observed, which manifest that the sculpture-reduction process hasn't introduced other surface groups, and correspond to the results of XPS.

Thus, the Ti^{3+} self-doping B-TiO₂/g-C₃N₄ hollow core-shell nano-heterojunction has been fabricated successfully.

The photocatalytic hydrogen production performance of the different samples is revealed in Fig. 7, including the TiO₂, TiO₂/g-C₃N₄, B-TiO₂/g-C₃N₄, B-TiO₂ and g-C₃N₄. As revealed, the normal TiO₂ nanospheres exhibit weaker H₂ production of ∼ 45.04 μmol/g·h, which could be ascribed to the intrinsic H₂ production performance of the TiO₂. It's evident that, with introducing of the g-C₃N₄ and the sculpture-reduction process, the hydrogen production performance exhibits an obvious enhancement and gets an optimal value at the B-TiO₂/g-C₃N₄ (∼ 808.97 μmol/g·h). By calculating, the hydrogen production performance of the B-TiO₂/g-C₃N₄ hollow core-shell nano-heterojunction is about 18 times than the normal TiO₂ nanospheres, which indicates that the B-TiO₂ and heterojunction would be the main factors for the photocatalytic hydrogen production enhancement. As a control group, the as-prepared B-TiO₂ and g-C₃N₄ are also carried out at the same condition. As displayed, there are about ∼ 474.34 and ∼ 12.37 μmol/g·h H₂ produce from the B-TiO₂ and g-C₃N₄ respectively, which would be valid evidences for that the nano-heterojunction could enhance the photocatalytic hydrogen production efficiently.

Based on the remarkable photocatalytic hydrogen production performance, it's significant to explore the cycling stability of the as-prepared B-TiO₂/g-C₃N₄ hollow core-shell nano-heterojunction. As shown in Fig. 8, in 30 h (6 consecutive cycles) hydrogen production process, the B-TiO₂/g-C₃N₄ nano-heterojunction exhibits a commendable stability and obtains a higher average of about 794.90 μmol/g·h, that closes to the initial value (808.97 μmol/g·h) and could be deemed as a comforting result. As shown in Fig. S3 (ESI), the XRD of the sample after reaction exhibits similar diffraction peaks as the initial sample, which

indicates that the as-prepared B-TiO₂/g-C₃N₄ nano-heterojunction obtains a prominent stability in the photocatalytic process.

All above results manifest that the sculpture-reduction process and nano-heterojunction could improve the photocatalytic hydrogen production performance and cycling stability efficiently. Thus, exploring the mechanism of the B-TiO₂/g-C₃N₄ nano-heterojunction in the photocatalystic hydrogen production process would be a significant issue.

Fig. 9 shows the UV–vis absorption spectra of the different samples. As reveled, the obviously absorption locates at approximately 380 nm could be ascribed to the intrinsic band gap of the normal TiO₂ [24–26]. With the introducing of g-C₃N₄, the absorption of the nano-heterojunction exhibits an obviously red-shift in visible light, which could be attributed to the absorption of the g-C₃N₄ and corresponds to the intrinsic absorption of the pure g-C₃N₄ [28,29]. Subsequently, with the sculpture-reduction process, the B-TiO₂/g-C₃N₄ nano-heterojunction exhibits an evident absorption in visible light, which is attributed to the Ti^{3+} and the O_v, and corresponds to the absorption of the pure B-TiO₂ [22,25,27,28]. It's obvious that the increasing absorption would be regarded as an important reason for the photocatalytic hydrogen production enhancement. It's interesting that the pure B-TiO₂ nanospheres exhibit stronger visible light absorption than the B-TiO₂/g-C₃N₄, while the optimal hydrogen production performance is obtained at the B-TiO₂/g-C₃N₄, which indicates that the nano-heterojunction at the interface would also play an important role in the photocatalytic hydrogen production.

In this core-shell nano-heterojunction, the separation and transfer of the photon-generated carriers would be important factors for the photocatalytic performance, and the transient photocurrent response and EIS (electrochemical impedance spectroscopy) Nyquist plots of the TiO₂, TiO₂/g-C₃N₄, B-TiO₂/g-C₃N₄, B-TiO₂ and g-C₃N₄ are reveled in Fig. 10. As revealed in Fig. 10a, with the deposition and sculpture-reduction process, the transient photocurrents of the samples exhibit an obvious enhancement under the continuously illumination switch on and off. By calculating, the transient photocurrents of each sample are
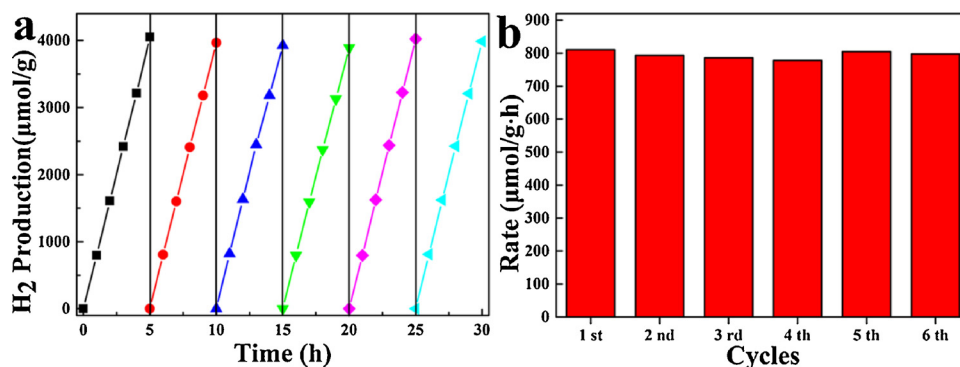

Fig. 8. (a) The cycle curve of the B-TiO₂/g-C₃N₄ hollow core-shell nano-heterojunction, (b) the histogram of the samples.
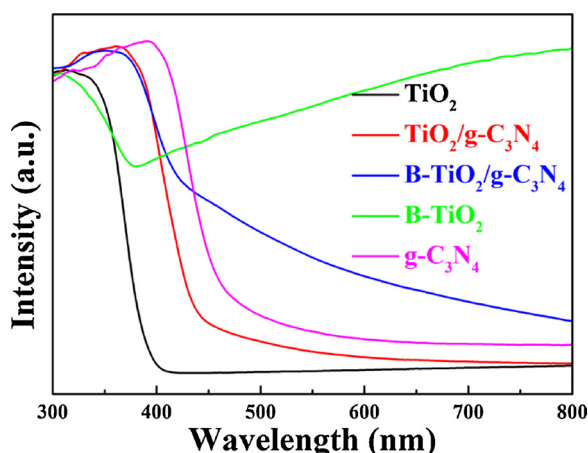
Fig. 9. The UV–vis absorption spectra of the TiO_2, TiO_2/g-C_3N_4, B-TiO_2/g-C_3N_4, B-TiO_2 and g-C_3N_4.

3.4×10^{-2} (TiO_2), 6.4×10^{-2} (TiO_2/g-C_3N_4), 24.1×10^{-2} (B-TiO_2/g-C_3N_4), 12.3×10^{-2} (B-TiO_2) and 1.8×10^{-2} (g-C_3N_4) µA, respectively. There, the increased photocurrent could be majorly ascribed to the efficient photo-generated separation and transferring, which is benefit for the photocatalysis and correspond to the results of photocatalytic performance [27,28,49]. Further, as demonstrated in Fig. 10b, the EIS Nyquist plots are deemed as another valid methods to investigate the migration and interface transfer/recombination rates of charge carriers [27,28,49]. As shown, the radius of the circular arc decreases with the deposition of the g-C_3N_4 and sculpture-reduction process, and obtains the smallest value at B-TiO_2/g-C_3N_4, which indicate the B-TiO_2/g-C_3N_4 obtains more eff ;ective separation of photo-generated carriers and higher efficiency of charge immigration across the heterojunction interface, that corresponds to the results of the transient photocurrent response. In addition, the PL is regarded as another important information to evaluate the separation of the photo-generated carriers [29]. As revealed in the Fig. S4 (ESI), the sample of B-TiO_2/g-C_3N_4 exhibits the lower PL than the g-C_3N_4 and TiO_2/g-C_3N_4, which indicate that the heterojunction modification and sculpture-reduction process could decrease the recombination of the photo-generated carriers efficiently and corresponds to the above results. From these above, including the transient photocurrent response, EIS Nyquist plots and PL, the B-TiO_2/g-C_3N_4 nano-heterojunction, with high photo-generated carrier separation and faster charge transfer, could increase the lifetime of the photo-generated carrier to improving the photocatalytic hydrogen production activity.

Moreover, the type of semiconductor and band potential of the g-C_3N_4 and B-TiO_2 are the basic factors for designing this nano-heterojunction. Thus, the electrochemical Mott-Schottky experiment is performed. There, based on the Mott-Schottky equation, the capacitance (C) depend on applied potential could be fitted as follows [50,51]:

$$\frac{1}{C^2} = \pm \frac{2}{e \varepsilon \varepsilon_0 N_d} \left(E - E_{FB} - \frac{K_b T}{e} \right)$$

where, the slope denotes the type of semiconductor (positive to n-type and negative to p-type) and the N_d denotes the carrier density. Further, the C, E (corrected by the AgCl vs 0.197 eV) and the intercept on the x-axis denote the space charge capacitance, applied potential and E_{fb} (band potential), respectively. As revealed in Fig. 11, the positive slope in the Mott–Schottky plot indicates that both of the g-C_3N_4 and B-TiO_2 are typical n-type semiconductors [51,52]. Furthermore, by calculating, the flat band potential of the g-C_3N_4 and B-TiO_2 are −0.95 (vs AgCl) and −0.66 eV (vs AgCl), respectively. Combined with the band gap of each other and corrected by the AgCl, the CB (conduction band) of g-C_3N_4 and TiO_2 could be calculated to be −0.75 eV (vs NHE) and −0.46 eV (vs NHE), and the valence band locate at 1.85 eV (vs NHE) and 1.98 eV (vs NHE), respectively. Compared with the Fig. S5 (ESI), the CB of the B-TiO_2 is more negative than the normal TiO_2, which is more benefit for the HER (hydrogen evolution reaction) and is an advantage of this B-TiO_2. Hence, it's obvious that the photon-generated electrons would transfer to the CB of TiO_2 and the photon-generated holes would transfer to the VB of g-C_3N_4 [27–29], which could promote the separation of the photon-generated carriers efficiently and is regarded as the unique advantage for this core-shell heterojunction structure.

Based on the above results, including the morphology, structure and electrochemistry test, the mechanism of the photocatalystic hydrogen production enhancement of the Ti^{3+} self-doping B-TiO_2/g-C_3N_4 hollow core-shell nano-heterojunction could be proposed as the Fig. 12, which could be ascribed to the Ti^{3+} and O_v in the B-TiO_2, interface nano-heterojunction and the hollow core-shell structure.

As reveled in Figs. 7 and 9, the B-TiO_2/g-C_3N_4 and B-TiO_2, with stronger visible light absorption, exhibit much preferable photo-catalystic hydrogen production than that of normal TiO_2, g-C_3N_4 or TiO_2/g-C_3N_4, which could be ascribed to the unique donor level of the O_v (O vacancy) and Ti^{3+} in the B-TiO_2 [21,24]. There, the O_v could form a new sublevel state at the bottom of the TiO_2 conduction band, which could increase the visible light absorption and speed up the photo-generated charge carrier separation for improving the visible light response [26–28], and is considered as an important reason for photocatalysis. Further, in the presence of adsorbed water, induced by the Ti^{3+}, the hydrogen atoms would diffuse into the TiO_2 to form a self-hydrogenated shell on the interface [22], which could reduce the activation barrier of the H_2, make the water protons to photo-excited stage and promote the hydrogen diffusing to the subsurface more easily for enhancing the hydrogen production [22,27,28,53,54], that is considered as one of the most important reasons for hydrogen production enhancement and has been proved by current researches [22]. In addition, the more negative CB of the B-TiO_2 would be one more advantage for HER. It's interesting that though the pure B-TiO_2
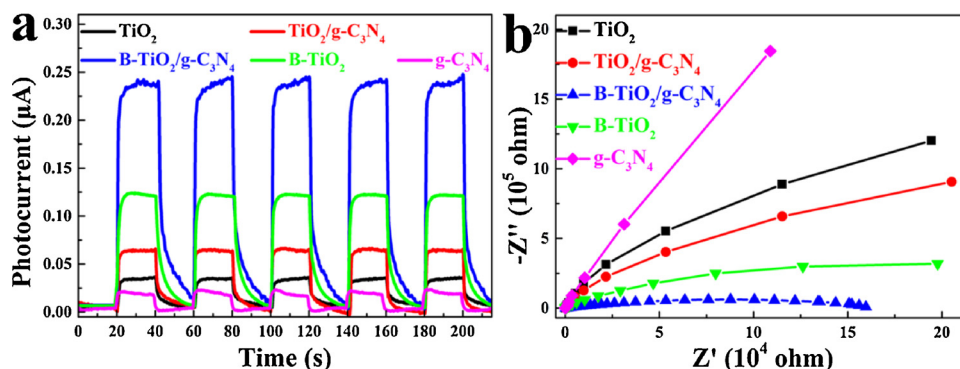

Fig. 10. (a) Transient photocurrent response and (b) EIS Nyquist plots of the TiO_2, TiO_2/g-C_3N_4, B-TiO_2/g-C_3N_4, B-TiO_2 and g-C_3N_4.
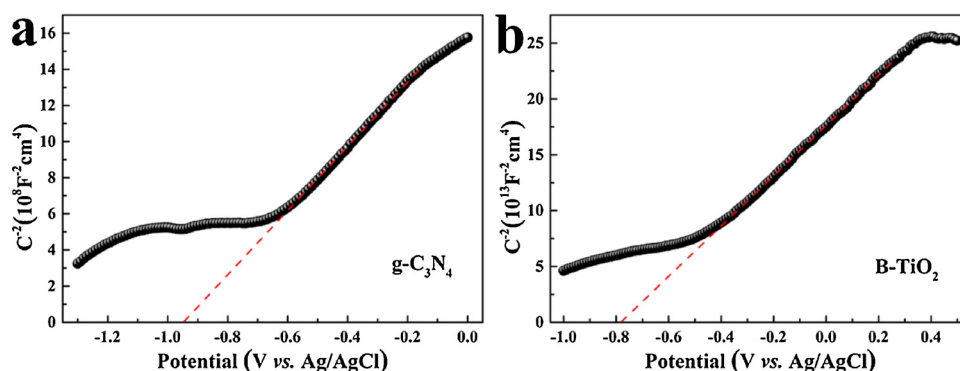
Fig. 11. The Mott-Schottky plots of the samples, (a) g-C$_3$N$_4$, (b) B-TiO$_2$.
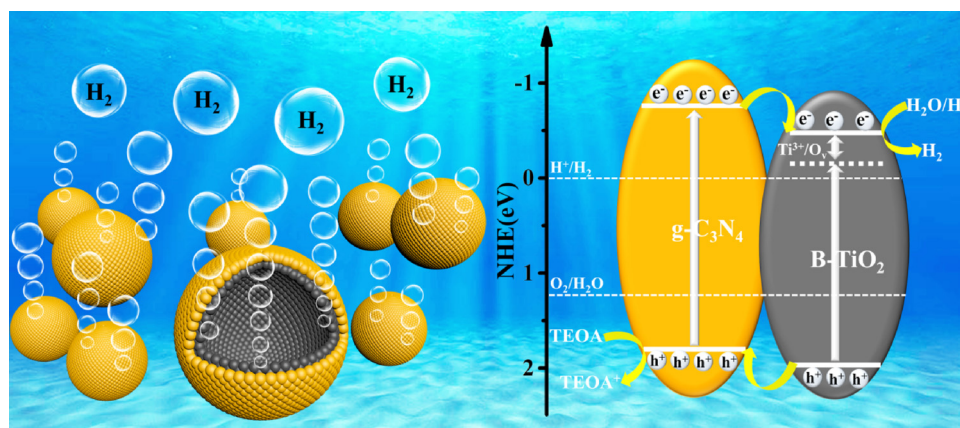

Fig. 12. The photocatalytic hydrogen production mechanism of the Ti^{3+} self-doping B-TiO$_2$/g-C$_3$N$_4$ hollow core-shell nano-heterojunction.

nanospheres obtain more intense absorption in visible light, but the B-TiO$_2$/g-C$_3$N$_4$ heterojunction exhibits more excellent photocatalytic hydrogen production (similar as the TiO$_2$/g-C$_3$N$_4$ and pure g-C$_3$N$_4$), which indicates that the nano-heterojunction would be another important reason for the enhancement. In such system, under illumination, driven by the internal electric field of the nano-heterojunction, the excited photon-generated electron (CB of g-C$_3$N$_4$) would transfer to the B-TiO$_2$ (CB of B-TiO$_2$) and the photon-generated holes (VB of B-TiO$_2$) would transfer to the g-C$_3$N$_4$ (VB of g-C$_3$N$_4$), which could provide a more efficient charge carriers separation for increasing the lifetime of the photon-generated carriers [28,29]. Incorporated with the induction of O$_v$ and Ti^{3+}, the long lifetime photon-generated electrons could reducing the H$^+$ much more efficiently to enhance the photocatalytic hydrogen production [22,28]. This process could be proved by the results of TEM, transient photocurrent, PL, EIS and Mott-Schottky plots, and is deemed as the most believable explanation for the enhanced photocatalytic hydrogen production.

Additionally, the hollow core-shell structure also plays a prominent role, because that the double walls could provide large specific surface areas (B-TiO$_2$/g-C$_3$N$_4$, 96.80 m^2/g) for the photocatalytic hydrogen production [43] and the hollow nanospheres could remain multiple reflections for increasing visible light utilization.

Thus, the Ti^{3+} self-doping B-TiO$_2$/g-C$_3$N$_4$ hollow core-shell nano-heterojunction exhibits obvious enhancement of photocatalytic hydrogen production performance under illumination.

4. Conclusions

We have successfully prepared the Ti^{3+} self-doping B-TiO$_2$/g-C$_3$N$_4$ hollow core-shell nano-heterojunction via simple hydrothermal deposition and sculpture-reduction processes. The as-prepared B-TiO$_2$/g-C$_3$N$_4$ hollow core-shell nano-heterojunction exhibits remarkable

photocatalytic enhancement towards the hydrogen production, with a catalytic activity nearly 18 times and 65 times than that of normal TiO$_2$ and g-C$_3$N$_4$, respectively. There, the O$_v$, Ti^{3+} self-doping and core-shell nano-heterojunction would be regarded as the main reasons, in which the O$_v$ could improve the visible light response, Ti^{3+} could induced the interface to form a self-hydrogenated shell for reducing the activation barrier of the H$_2$, and the core-shell heterojunction could drive the transfer of photon-generated carriers to promote the photon-generated carrier separation, those could reducing the H$^+$ efficiently to enhance the photocatalytic hydrogen production. What's more, the abundant specific surface areas of the hollow core-shell nanospheres would be another reason. Additionally, the photocatalyst exhibits remarkable photocatalytic stability in continuous photocatalysis.

Thus, the design of the Ti^{3+} self-doping B-TiO$_2$/g-C$_3$N$_4$ hollow core-shell nano-heterojunction would provide a new sight for designing the potential hydrogen production materials.

Acknowledgments

Appendix A. Supplementary data

Supplementary material related to this article can be found, in the online version, at doi:https://doi.org/10.1016/j.apcatb.2018.09.079.

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